**[P₆Se₁₂]⁴⁻: A Phosphorus-rich Selenophosphate
with Low-valent P Centers.**

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Supplementary Information

Fig. 1S: Solid state optical absorption spectrum of $\text{Rb}_4\text{P}_6\text{Se}_{12}$.

Fig. 2S: Infrared absorption spectrum of $\text{Rb}_4\text{P}_6\text{Se}_{12}$.

Fig. 3S: Fourier transform Raman spectrum of $\text{Rb}_4\text{P}_6\text{Se}_{12}$.

Solid-state UV-vis/Near IR Spectroscopy. Optical diffuse reflectance measurements were made at room temperature using a Shimadzu UV-3101 PC double beam, double-monochromator spectrophotometer operating in the 200-2500 nm region. The instrument is equipped with an integrating sphere and controlled by a personal computer. BaSO_4 was used as a 100% reflectance standard. The sample was prepared by grinding the crystals intimately to a powder and spreading it on a compacted surface of the powdered standard material, preloaded into a sample holder. The reflectance versus wavelength data generated were used to estimate the band gap of the material by converting reflectance to absorption data.

Infrared Spectroscopy. FT-IR spectrum was recorded as solids in a CsI matrix. The crystals were ground with dry CsI into a fine powder and pressed into translucent pellets. The spectrum was recorded in the far-IR region ($600\text{--}100\text{ cm}^{-1}$, 4 cm^{-1} , resolution) with the use of a Nicolet 740 FT-IR spectroscopy equipped with a TGS/PE detector and silicon beam splitter.

Raman Spectroscopy. Raman spectrum was recorded on a Holoprobe Raman spectrograph equipped with a CCD camera detector using 633 nm radiation from a HeNe laser for excitation and a resolution of 4 cm^{-1} . Laser power at the sample was estimated to be about 5 mW, and the focused laser beam diameter was ca. $10\text{ }\mu\text{m}$. A total of 128 scans was sufficient to obtain good quality spectra.